

## **METHOD AND APPARATUS FOR MAKING CRYSTALS WITHOUT A PRE-MELT STEP**

### **Background of Invention**

[0001] The invention relates to methods and apparatus for making crystals. While not wishing to be bound to a particular group of crystals, it is convenient in the following discussion to focus on a particular group of crystals. One group of crystals of interest is optical fluoride crystals. Single-grained optical fluoride crystals are useful in applications requiring transmission at short wavelengths, e.g., in the vacuum ultraviolet region. At present,  $\text{CaF}_2$  crystal is the most viable lens material for 157-nm microlithography.

[0002] Optical fluoride crystals as well as other types of crystals can be grown in two steps. The first step is a pre-melt step in which crystal raw material in powder or granular form is melted and then rapidly cooled into a solid body, which herein will be referred to as a crystal pre-melt. The second step is a growth step in which the crystal pre-melt is melted and then used to grow one or more crystals.

[0003] Single-grained crystals are commonly grown using the Bridgman-Stockbarger process. As illustrated in Figure 1A, the Bridgman-Stockbarger process takes place in a vertical furnace 100 having an upper zone 102 and a lower zone 104. A middle or thermal gradient zone 106 is defined between the upper zone 102 and the lower zone 104 by making the temperature of the upper zone 102 higher than the temperature of the lower zone 104. The growth step starts with loading of a crystal pre-melt 108 into a crystal growth crucible 110. With the growth crucible 110 in the upper zone 102, the upper zone 102 is then heated to a temperature sufficient to melt the crystal pre-melt 108. After melting the crystal pre-melt 108, the growth crucible 110 is lowered from the upper zone 102, through the thermal gradient zone 106, into the lower zone 104. As shown in Figure 1B, as the growth crucible 110 passes through the thermal gradient zone 106, a phase transition occurs inside the molten crystal pre-melt 108a, creating a crystal front 112. The crystal front 112 propagates inside the growth crucible 110, within the molten crystal pre-melt 108a, as long as the growth crucible 110 continues to move downwardly into the lower zone 104.

[0004] Returning to Figure 1A, the crystal pre-melt 108 is made by subjecting relatively pure crystal raw material in powder or granular form to a pre-melt step. The main purpose of the

pre-melt step is to increase the bulk density of the crystal raw material so that the volume of the crystal growth furnace can be used efficiently. For example, synthetic  $\text{CaF}_2$  powder has an apparent density of  $1.1 \text{ g/cm}^3$ , and crystals grown from  $\text{CaF}_2$  powder have an apparent density that is close to the theoretical density of  $\text{CaF}_2$ , i.e.,  $3.18 \text{ g/cm}^3$ . Thus, if synthetic  $\text{CaF}_2$  powder is used directly as the crystal raw material, two-thirds of the volume of the crystal growth furnace will not be used, or at least, not used efficiently. Through a pre-melt step, the apparent density of the  $\text{CaF}_2$  raw material can be increased to approximately  $2.2 \text{ g/cm}^3$ , which would be much closer to the density of the grown  $\text{CaF}_2$  crystal.

[0005] The pre-melt step typically includes a treatment step in which oxide impurities are scavenged from the crystal raw material prior to melting the crystal raw material.

Commonly, the treatment step involves mixing a solid fluorinating agent, e.g.,  $\text{PbF}_2$ ,  $\text{ZnF}_2$ , or polytetrafluoroethylene (PTFE), with the crystal raw material and then heating the mixture to the melting point of the crystal raw material. At this temperature, the solid fluorinating agent reacts with oxides in the crystal raw material to form volatile gases that escape from the crystal raw material. However, use of solid fluorinating agent to scavenge oxide impurities has a drawback in that impurities such as  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ , or C can remain in the crystal raw material after treatment. For optical fluoride crystals, the presence of these impurities, even at trace levels, can result in absorption bands that are detrimental to transmission at wavelengths below 200 nm.

[0006] Recently, gaseous fluorinating agents, such as  $\text{CF}_4$ , HF,  $\text{SF}_6$ , and  $\text{BF}_3$ , have been proposed as alternatives to solid fluorinating agents in scavenging oxide impurities. With gaseous fluorinating agents, the risk of leaving harmful impurities such as  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ , or C in the grown crystal is relatively low or non-existent. However, use of gaseous fluorinating agents in scavenging oxide impurities in conventional settings poses various challenges. For example, the furnace and furnace elements, e.g., crucibles, thermocouples, and resistors, used in the pre-melt step are typically made of pure graphite or other materials that are susceptible to corrosion by the gaseous fluorinating agents, especially in the presence of oxygen atmosphere and/or at elevated temperatures. For example,  $\text{CF}_4$  attacks thermocouples at temperatures above  $1100^\circ\text{C}$ . Further, pure graphite is porous and tends to outgas. Outgassing of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , or CO from the graphite parts may contribute to contamination of the crystal pre-melt after treatment.

[0007] The pre-melt step typically takes between 12 and 15 days, occupying a furnace that could otherwise be used for actual growth of the crystals and thus hampering productivity. To facilitate melting of the crystal pre-melt during the crystal growth step, the crystal pre-melt typically has to be crushed before it is loaded into the crystal growth crucible. This crushing action is often a source of metallic and other forms of contamination in the grown crystal. Further, the growth furnace is open to air while the crystal pre-melt is being loaded into the growth furnace. This exposure can be an additional source of contamination.

[0008] From the foregoing, there is desired a method of making crystals that minimizes or eliminates one or more of the aforementioned concerns.

### **Summary of Invention**

[0009] In one aspect, the invention relates to a method of making crystals which comprises suspending a porous preform made of a crystal raw material in a hermetically-sealed chamber, heating the porous preform to a selected treatment temperature that enables reaction between a fluorinating agent and oxide impurities in the porous preform, reacting the fluorinating agent with the oxide impurities at the selected temperature for a selected time period, forming a melt from at least a portion of the porous preform, filling a crucible in the hermetically-sealed chamber with the melt, and progressively moving the melt through a temperature gradient zone defined inside the hermetically-sealed chamber to grow one or more crystals.

[0010] In another aspect, the invention relates to an apparatus for making crystals which includes a hermetically-sealed muffle furnace made of a non-porous refractory material, at least one port for entry and exit of gaseous substance within the muffle furnace, at least two temperature-controlled zones defined inside the muffle furnace, a crystal growth crucible disposed inside the muffle furnace, an actuator operable to translate the crucible along a length of the muffle furnace, and means for suspending a porous preform above the crucible.

[0011] Other features and advantages of the invention will be apparent from the following description and the appended claims.

### **Brief Description of Drawings**

[0012] Figures 1A and 1B illustrate a prior-art method of growing a crystal.

[0013] Figure 2A is a schematic of an apparatus for making crystals according to one embodiment of the invention.

[0014] Figure 2B shows an apparatus for making oriented crystals according to another embodiment of the invention.

[0015] Figure 2C shows a porous preform being melted into a waiting crucible in a muffle furnace in accordance with one embodiment of the invention.

[0016] Figure 2D shows molten material moved through a temperature gradient zone in a muffle furnace to grow one or more crystals.

### **Detailed Description of Preferred Embodiments**

[0017] The invention will now be described in detail with reference to a few preferred embodiments, as illustrated in accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the invention. However, it will be apparent to one skilled in the art that the invention may be practiced without some or all of these specific details. In other instances, well-known features and/or process steps have not been described in detail in order to not unnecessarily obscure the invention. The features and advantages of the invention may be better understood with reference to the drawings and discussions that follow.

[0018] Embodiments of the invention provide an apparatus and a method for making crystals from crystal raw material without a pre-melt step. The apparatus includes a muffle furnace made of a non-porous refractory material. Treatment of crystal raw material to remove oxide impurities and growing of crystals from the treated material all occur in the muffle furnace; therefore, the treated material is not open to air prior to being used in growing the crystals. By constructing the muffle furnace from a non-porous refractory material, the crystal raw material is protected from contamination after treatment through outgassing of the muffle furnace material.

[0019] The type of crystals made by the method and apparatus of the invention would depend on the composition of the crystal raw material from which the crystals are made. One group of crystal raw material that is of interest herein is fluoride crystal raw material. In one embodiment, the fluoride crystal raw material includes a metal fluoride selected from the

group consisting of  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{MgF}_2$ ,  $\text{SrF}_2$ ,  $\text{LiF}$ ,  $\text{NaF}$ ,  $(\text{M}_1)_x(\text{M}_2)_{1-x}\text{F}_2$ , and  $\text{M}_3\text{AlF}_6$ , and mixtures thereof, where  $\text{M}_1$  is selected from the group consisting of Li and K;  $\text{M}_2$  is selected from the group consisting of Ca, Ba, Mg, and Sr;  $\text{M}_3$  is selected from the group consisting of Li, Na, K, Rb, and Cs; and  $x$  is in the range from 0 to 1, preferably in a range from 0.01 to 0.99. The fluoride crystal raw material may also include mixed metal fluorides wherein a metal fluoride selected from the lanthanide series, for example, lanthanum, ytterbium, yttrium, or others of the series, is used as one of  $\text{M}_1$  or  $\text{M}_2$ , or is used in addition to  $\text{M}_1$  and  $\text{M}_2$ . Those skilled in the art will recognize the possible combinations. Optionally, a small amount of a solid fluorinating agent, e.g., 0.5 to 2 wt% of  $\text{PbF}_2$ ,  $\text{ZnF}_2$ , or other solid fluorinating agent, may be mixed with the fluoride crystal raw material.

[0020] Figure 2A shows an apparatus 200 for making one or more crystals without a pre-melt step in accordance with one embodiment of the invention. The apparatus 200 includes a muffle furnace 202 that is constructed from a non-porous refractory material. Examples of suitable non-porous refractory materials include quartz, alumina, silicon carbide, vitreous carbon, vitreous graphite, glassy carbon-coated graphite, and a combination of these materials. These materials are also inert in that they are not expected to react with the process gases under the process conditions in which crystal raw material will be treated and formed into crystals inside the muffle furnace 202. By constructing the muffle furnace 202 from a non-porous refractory material, the crystals made inside the muffle furnace 202 are protected from contamination through outgassing of the muffle furnace material.

[0021] The upper and lower ends of the muffle furnace 202 are covered with end caps 204, 206, respectively. Preferably, the end caps 204, 206 make a sealed contact with the muffle furnace 202, providing a hermetically-sealed environment inside the muffle furnace 202. A variety of sealing mechanisms, such as metal-to-metal seal, O-ring seal, etc., can be used between the muffle furnace 202 and the end caps 204, 206 to achieve the sealed contact. To avoid contamination of the crystal raw material after treatment through outgassing of the end cap material, the end caps 204, 206 are also preferably constructed from a non-porous refractory material, such as listed above for the muffle furnace 202.

[0022] Either or both of the end caps 204, 206 or the wall of the muffle furnace 202 may include one or more ports through which gases can flow into and out of the muffle furnace 202. For example, as illustrated in Figures 2A-2D, an inlet port 212 is provided in the end cap 204. The inlet port 212 may be selectively connected to gas sources 214, 216. As an

example, the gas source **214** could contain a gaseous fluorinating agent, and the gas source **216** could contain an inert gas. Valves **215** may be provided to control rate of flow from the gas sources **214**, **216** into the muffle furnace **202**. As also illustrated in Figures 2A-2D, an outlet port **218** is also provided in the end cap **204**. The outlet port **218** may be connected to an effluent treatment chamber **220**, which may include a scrubber (not shown) to remove or decompose any gaseous fluorinating agent in the effluent of the muffle furnace **202**.

Examples of scrubbers include heated metal oxide such as soda lime or a plasma system.

Although not shown, a vacuum system could also be incorporated to suck out gas from the muffle furnace **202** through the outlet port **218**.

[0023] In one embodiment, a crucible stack **222** is supported inside the muffle furnace **202**. The crucible stack **222** may include any number of crucibles or crystal growth chambers **224** stacked vertically. Typically, the number of crucibles or crystal growth chambers in the crucible stack **222** can range from 1 to 20. The crucible stack **222** may be made of a refractory material that may be porous or non-porous. Preferably, the crucible stack **222** is made of a non-porous refractory material, such as previously listed for the muffle furnace **202**. As shown in Figure 2A, the crucibles **224** in the stack **222** communicate through holes **226** in their bottom walls. As shown in Figure 2B, the crucible **224** at the bottom of the stack **222** may include a seed crystal holder **228** at its base. The seed crystal holder **228** is for receiving a seed crystal **230** having a specific crystallographic orientation and is needed only if an oriented crystal is to be grown. In practice, the seed crystal **230** would be selected to have a similar phase and melting point as the crystal to be grown.

[0024] Returning to Figure 2A, a lift mechanism **232** is coupled to the crucible stack **222**. As an example, the lift mechanism **232** could be a fluid-powered actuator, such as a hydraulic or pneumatic actuator, or a mechanical actuator. When operated, the lift mechanism **232** translates the crucible stack **222** along an axial length of the muffle furnace **202**. The lift mechanism **232** may also have a capability to rotate the crucible stack **222** inside the muffle furnace **202**. In one embodiment, the lift mechanism **232** includes a sliding member **234**, such as a piston or rod, which extends from the outside into the muffle furnace **202** through the end cap **206**. Preferably, one or more seals (not shown) are fitted between the sliding member **234** and the end cap **206** to maintain the gas-tight environment inside the muffle furnace **202**, particularly while the crystal material is being processed inside the muffle furnace **202**.

[0025] Different temperature zones can be defined inside the muffle furnace 202 through the use of one or more heaters. For example, a variable temperature heater 236 is positioned adjacent or around an upper section of the muffle furnace 202 to define an upper (treatment/melting) zone 240 inside the muffle furnace 202. Also, a variable temperature heater 238 is positioned adjacent or around a lower section of the muffle furnace 202 to define a lower (cooling/annealing) zone 242 inside the muffle furnace 202. The heaters 236, 238 can be independently controlled to maintain different temperatures in the upper and lower zones 240, 242, respectively. A middle temperature-gradient zone 244 is defined between the upper zone 240 and the lower zone 242 when the temperatures in the upper and lower zones 240, 242 are different. Typically, a heater is not positioned around or adjacent the middle zone 244, and the desired temperature gradient in the middle zone 244 is achieved primarily by adjusting the temperatures in the zones 240, 242.

[0026] More than two heaters can be positioned adjacent or around different sections of the muffle furnace 202 to allow further refinement of the temperature zones in the muffle furnace. Alternatively, one or more heaters may be translated along the length of the muffle furnace 202 to achieve the desired temperature zones in the muffle furnace. In addition, each of the heaters 236, 238 can have one or more heating elements, each of which can be independently controlled in order to form a temperature gradient within the upper or lower zone 240, 242 if so desired. This feature is particularly useful with regard to the lower zone heater 238 when annealing is to be carried out within the lower zone 238 as the crucible stack 222 is lowered. The heaters 236, 238 are preferably mounted outside of the muffle furnace 202 to prevent them from contaminating the crystal raw material processed inside the muffle furnace and to prevent them from being damaged by the process gases.

[0027] Although not shown, insulation material may be disposed between the heaters 236, 238 to allow greater control over the temperature profile in the temperature gradient zone 244. Insulation material could also be provided around the outside of the heaters 236, 238 to contain heat around the muffle furnace 202. The temperature in the upper and lower zones 240, 242 can be measured using thermocouples 245, 246, respectively, and the output of the thermocouples 245, 246, respectively, can be used to control the power delivered to the heaters 236, 238 so that desired temperatures are maintained in the upper and lower zones 240, 242. To avoid contact between the thermocouples 245, 246 and process gases in the muffle furnace 202, the thermocouples may be mounted on the outside wall of the muffle

furnace 202 instead of inside the muffle furnace. In an alternate embodiment, the sealed muffle furnace 202 could be inserted into a conventional furnace, wherein the conventional furnace includes the furnace elements, e.g., heaters, necessary to provide the desired temperature zones in the muffle furnace.

[0028] The invention is not limited to the use of an external heat source, such as heaters 236, 238, to provide a desired temperature profile in the upper and lower zones 240, 242.

Inductive heating or resistive heating could also be used to provide the desired temperatures in the upper and lower zones 240, 242. For example, in a situation where the muffle furnace is made of a conductive non-porous refractory material, such as vitreous graphite, vitreous carbon, or silicon carbide, the muffle furnace 202 could be used as an electromagnetic induction susceptor when coupled with an induction coil. Alternatively, the muffle furnace 202 itself could serve as a heating element if a controlled current is placed across it.

[0029] Referring to Figure 2A, a method of making one or more crystals includes suspending a porous preform 250 made of crystal raw material, such as fluoride crystal raw material, in the upper zone 240 of the muffle furnace 202, above the crucible stack 222. In one embodiment, the porous preform 250 is suspended by a handle 252 having one end attached to the porous preform 250 and the other end coupled to the end cap 204. The handle 252 could be made of a crystal or a non-porous refractory material, such as listed above for the muffle furnace material. Alternatively, the porous preform 250 could be held by, for example, a claw-like device (not shown) grasping the outside of the preform 250. The claw-like device is such that it exerts continuous pressure on the porous preform 250 so that the preform is held in position above the crucible stack 222 during the treatment and melting steps.

[0030] In one embodiment, the porous preform 250 is made by isostatic pressing of crystal raw material, as taught by Malcolm Ivy in U.S. Patent Application Serial No. 10/611,506 (assigned to Corning Incorporated). Briefly, the process for forming the porous preform 250 includes loading relatively pure crystal raw material in powder form into a flexible mold and then applying isostatic pressure to the mold to compress the crystal raw material. The isostatic pressing could be cold, warm, or hot. The handle 252 could be inserted in the top of the crystal raw material so that it is molded to the top of the crystal raw material during the isostatic pressing. Alternatively, a notch can be cut at the top of the porous preform 250 after



isostatic pressing, and the handle **252** can be inserted in the notch to facilitate handling of the porous preform **250**.

[0031] Treatment of the porous preform **250** to remove oxide impurities can begin once the porous preform **250** is suspended in the upper zone **240** of the muffle furnace **202** and the muffle furnace **202** is hermetically sealed. Treatment may be with a solid fluorinating agent already in the porous preform **250** and/or with a gaseous fluorinating agent that will be introduced into the muffle furnace **202**. Before reacting the solid and/or gaseous fluorinating agent with the porous preform **250**, the muffle furnace **202** is purged and filled with an inert gas, such as argon, helium, or nitrogen. Alternatively, any gas in the muffle furnace **202** may be evacuated before filling the furnace **202** with the inert gas. As the muffle furnace **202** is filled with the inert gas, the muffle furnace **202**, which is initially at room temperature, is heated to a treatment temperature. The treatment temperature should be high enough to enable reaction between the solid or gaseous fluorinating agent and the porous preform **250**. To facilitate diffusion of gases through the porous preform **250**, the treatment temperature should not be so high as to significantly increase the density of the preform. Heating to treatment temperature can occur in one step or in multiple steps.

[0032] In one embodiment, when the treatment temperature is reached, a solid fluorinating agent already embedded in the porous preform **250** reacts with oxide impurities in the porous preform **250** to produce volatile gases, which are carried away to the treatment chamber **220** through the outlet port **218**.

[0033] In another embodiment, when the treatment temperature is reached, the inert gas in the muffle furnace **202** is replaced with a gaseous fluorinating agent, such as  $\text{CF}_4$ ,  $\text{NF}_3$ ,  $\text{SF}_6$ ,  $\text{BF}_3$ ,  $\text{C}_2\text{F}_4$ ,  $\text{HF}$ ,  $\text{F}_2$ , or a mixture of these fluorides. The gaseous fluorinating agent may be carried into the muffle furnace **202** in a stream of inert gas, such as argon, helium, or nitrogen. The amount of gaseous fluoride in the inert gas stream may be in a range from 1% to 100% by weight. The inert gas may be premixed with the gaseous fluorinating agent or provided from a separate source. In one embodiment, the flow rate of the gaseous fluorinating agent is adjusted such that the pressure in the muffle furnace **202** is in a range from 0.1 to 5 atm, preferably around 1 atm. The gaseous fluorinating agent is selected based on its decomposition temperature and the melting point of the crystal material. For example,  $\text{CF}_4$  has a high bond energy (536 KJ/mol) and is expected to be an effective oxide scavenger at temperatures of 1000°C and above and is better suited for treatment of high-melting

materials such as  $\text{CaF}_2$ ,  $\text{NF}_3$  and  $\text{SF}_6$  are expected to produce similar scavenging effect as  $\text{CF}_4$  at temperatures closer to 200 to 400°C and 500 to 800°C, respectively, and are thus better suited for the treatment of low-melting materials. In one embodiment, the treatment temperature is selected to be in the range of approximately 50 to 500 °C below the melting point of the material being purified.

[0034] The porous preform **250** is exposed to the gaseous fluorinating agent for a time period, for example, 1 to 240 hours, preferably 1 to 100 hours. During this period, the gaseous fluorinating agent reacts with oxide impurities in the porous preform **250** to produce volatile gases, which are carried away to the treatment chamber **220** through the outlet port **218**. Because there is no crucible in the flow path of the gaseous fluorinating agent and the porous preform **250**, the gaseous fluorinating agent can diffuse through the porous preform **250** without delay, reducing process time. Further, contamination of the porous preform **250** from crucible material is avoided. Further, the crucible stack **222** below the porous preform **250** is purified by the gaseous fluorinating agent while the porous preform **250** is being purified. The purified crucible stack **222** will later be used to grow the crystal(s).

[0035] The amount of oxide impurities removed from the porous preform **250** depends on the exposure time and treatment temperature. In general, the time required to remove oxide impurities decreases as treatment temperature increases. Also, the closer the treatment temperature is to the melting point of the crystal material, the shorter the time required to reduce the oxide impurity level of the crystal material. Gas analysis of the effluent from the muffle furnace **202** is used to determine the completion of the treatment step. For example, the oxygen concentration of the muffle furnace effluent may be measured, and when this oxygen concentration falls below a predetermined threshold, the treatment process can be stopped.

[0036] When the treatment process is completed, the muffle furnace **202** is purged with an inert gas, such as argon, helium, or nitrogen, or degassed to vacuum pressure (e.g.,  $10^{-5}$  torr or less). Then, the porous preform **250** is partially or entirely melted into the waiting crucible stack **222**. The ability to partially melt the porous preform **250** opens possibilities for growing crystals in batches inside the muffle furnace **202**. The porous preform **250** could be melted in-situ in the upper zone **240** by increasing the temperature in the upper zone **240** above the melting point of the crystal material. Alternatively, a separate melting zone may be provided inside the muffle furnace **202** in which the porous preform **250** can be melted into

the waiting crucible stack **222**. In Figure 2C, the crucible stack **222** is moved into the upper zone **240** to receive the molten material **254** formed by melting of the porous preform **250**. The crucibles **224** are filled from the bottom to the top as opposed to the top-down melting used in current crystal growth processes, which means that fewer voids will be trapped in the molten material **254**.

[0037] In Figure 2D, the crucible stack **222** with the molten material **254** is slowly translated from the upper zone **240** through the temperature gradient zone **244** into the lower zone **242**. As an example, the translation speed of the crucible stack **222** could be in a range from 0.5 mm/hr to 5 mm/hr. The temperature gradient zone **244** is formed by making the temperature in the lower zone **242** lower than the temperature in the upper zone **240**. As the crucible stack **222** passes through the temperature gradient zone **244**, a solid-liquid growth front **256** is created by a phase transition inside the molten material **254**. The solid-liquid growth front **256** propagates inside the crucible stack **222**, within the molten material **254**, as long as the crucible stack **222** continues to move downwardly into the lower zone **242**. The solid-liquid growth front **256** can be initially formed on an oriented seed crystal (not illustrated in Figure 2D, see Figure 2B) so that it conforms to the crystallographic orientation of the seed crystal as it propagates inside the crucible stack **222**. As is well known in the art, the grown crystal can be cooled or annealed in the lower zone **242** using a variety of cooling schedules. If the birefringence of the cooled or annealed crystal is not low enough, the crystal may be further annealed in a separate annealing furnace.

[0038] The invention provides many advantages. The invention bypasses the pre-melt step of the current crystal growth processes and integrates treatment of crystal raw material with the crystal growth step. This method of making crystals reduces contamination of the crystal raw material used in growing the crystal and frees up furnaces used for pre-melting in the current crystal growth processes. The present invention eliminates the need for a pre-melt crucible to hold crystal raw material. Instead, the crystal raw material is provided in the form of a porous preform that can be suspended and processed while being suspended. Without the pre-melt crucible in the way, quicker diffusion of gaseous fluorinating agent through the porous preform is enabled and contamination of the porous preform with crucible material is avoided.

[0039] High throughput is enabled by using a crucible stack with multiple crucibles or crystal growth chambers. Crystals can be grown in batches through a series of partial melting of

porous preform and growing of one or more crystals from the melt. The porous preform is purified in a muffle furnace in that is made of a non-porous inert material. Thus, the porous preform is not susceptible to contamination through outgassing of the muffle furnace material. Furnace elements such as thermocouples and heaters can be mounted on the outside of the muffle furnace to prevent them from contaminating the porous preform and/or from being attacked by the process gases.

**[0040]** The level of process control over temperature, pressure, and process gas is better in the hermetically-sealed muffle furnace environment than in a porous graphite furnace. There is ability to both pressurize the muffle furnace for the treatment step and provide a vacuum for the growth step. There is potential to provide an inert gas environment for growth versus requiring a vacuum. This reduces waiting time for good vacuum, and the heat capacity and conductivity of the inert gas would provide more temperature uniformity around the crystal. There is ability to start the liquid filling of the growth crucible from the bottom up versus the top down melting provided today. This filling method traps less voids and enables better outgassing and zone refinement of contamination.

**[0041]** While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.